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# Biaxiality of Liquid Crystal Formed by Bent-Core Molecules with a Transverse Dipole Moment Deviating from their Angular Bisector \*

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Monte Carlo simulations are performed to study the phase diagram of liquid crystals formed by bent-core molecules with a strong transverse dipole moment deviating from their angular bisector. The results show that the strong dipolar interaction, after suppressing uniaxial phases, encourages biaxiality, which leads to a Landau point or even to a Landau line in the phase diagram, inducing a more stable biaxial nematic phase. It is also found that a deviation of dipole moment from the angular bisector also suppresses uniaxiality in the small bend-angle regime.

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Liquid crystals as functional materials have been widely used in electro-optic display devices for many years, and recently researchers began to show interests in biaxial nematic liquid crystals because of their potential applications in fast-switching display devices.<sup>[1]</sup> In fact, the prediction of biaxial nematic phase can be dated back to as early as 1970s when Freiser<sup>[2]</sup> used a molecular field theory to show that molecules deviating from cylindrical symmetry should result in a biaxial nematic phase in addition to the uniaxial one. Since then, it has become the topic of a series of theoretical, computational and experimental studies, among which theoretical methods such as mean field theory (MFT),<sup>[3–5]</sup> bifurcation analysis,<sup>[6]</sup> density functional theory,<sup>[7]</sup> statistical theory<sup>[8,9]</sup> have been proved to be useful approaches. All of the theories mentioned above, as well as computer simulations,<sup>[10–13]</sup> suggested that the system should exhibit a biaxial nematic phase. While, in experiments, stable biaxial phases have been observed in lyotropic systems in 1980<sup>[14]</sup> and in polymeric systems in 2004.<sup>[15]</sup> However, its existence in thermotropic systems was not confirmed<sup>[16,17]</sup> until 2004 when Madsen *et al.*<sup>[18]</sup> and Acharya *et al.*<sup>[19]</sup> announced that bent-core molecules may form an elusive biaxial nematic phase. Recently the electric field effects of such kinds of bent-core molecules have also been studied in experiments.<sup>[20,21]</sup> Meanwhile theoretical studies using models for bent-core molecules<sup>[22–24]</sup> and computer simulations<sup>[25,26]</sup> all supported the typical phase diagram which consists of four phases: two uniaxial nematic ( $N_U$ ) phases, a biaxial nematic ( $N_B$ ) phase, and an isotropic ( $I$ ) phase. Especially, it was reported that the Landau point at which the isotropic phase undergoes a transition directly to the biaxial nematic phase occurs at a single tetrahedral angle of  $109.47^\circ$ . However, Madsen's<sup>[18]</sup> candidate molecule has a much larger angle of about  $140^\circ$  at which theoretically no biaxial nematic phase is predicted. We should note here that the type of molecules they considered have a strong transverse electric dipole mo-

ment, which may account for the deviation. To explore how a large transverse dipole moment in bent-core molecules influences the phase behaviors, Osipov *et al.*<sup>[27]</sup> used molecular theory while Bates<sup>[28]</sup> performed a series of Monte Carlo (MC) simulations based on a lattice model for bent-core molecules with a transverse dipole bisecting the bend angle. The results showed that the isotropic to the biaxial nematic phase transition is no longer restricted to a single angle but occurs at a range of angles. The Landau point extends into a Landau line and along this line, the  $I-N_B$  transition becomes first-order rather than continuous. Meanwhile, another kind of bent-core molecule with an oxazole heterocycle core shifting the dipole moment away from the bisector of the bent-core apex has been investigated experimentally by Acharya *et al.*<sup>[19]</sup> Now the question is: does the electric dipole moment fall into the direction of the bent-core angular bisector? To address this question, we carry out a series of Monte Carlo simulations for liquid crystals formed by asymmetric bent-core molecules with a strong transverse dipole moment deviating from their angular bisector.

As a simple prototype model, the Lebwohl-Lasher model<sup>[29]</sup> has been extremely successful in reproducing the behaviors of the uniaxial nematic phase. It has been extended to explore the phase behaviors of symmetric and nonsymmetric bent-core molecules,<sup>[25]</sup> including the phase diagram of bent-core molecules with a transverse dipole moment bisecting the bend angle.<sup>[28]</sup> Here we consider a more general case in which the molecular dipole moment does not point along the bent-core angular bisector but rather shift at an angle from it.

As shown in Fig. 1, each molecule is assumed to have two identical rods (rods 1 and 2) jointed at a fixed angle  $\theta$ . It is placed in a frame of three orthogonal axes, denoted by  $\{x, y, z\}$ . To simplify our calculation, we place the bent-core molecule in the  $yz$  plane in which  $y$  axis bisects the bent-core molecule while  $x$  axis is normal to it. The dielectric asymmetry of a core

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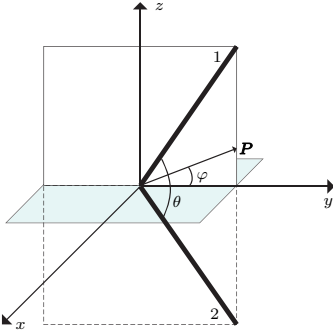
apex like the oxazole heterocyclecore in Ref. [18] generates an equivalent permanent dipole moment deviating from the angular bisector  $y$ . The angle between the direction of the electric dipole moment and  $y$  axis is denoted by  $\varphi$ . Each molecule is assumed to interact with its six nearest-neighbor molecules on a cubic lattice, as in the Lebwohl-Lasher model. The interaction energy between molecule  $i$  and its six nearest molecules is given by

$$U_i = \sum_{j=1}^6 (U_{ij}^{\text{anis}} + U_{ij}^{\text{dd}}), \quad (1)$$

where  $U_{ij}^{\text{anis}}$  is the anisotropic potential between molecules  $i$  and  $j$  written as

$$U_{ij}^{\text{anis}} = - \sum_{a=1,2} \sum_{b=1,2} \epsilon P_2(\cos \beta_{i_a j_b}). \quad (2)$$

Here the indices  $a$  and  $b$  run over the two rods in molecules  $i$  and  $j$ , respectively;  $\epsilon$  is the scaling energy parameter which is assumed to be a positive constant when the molecules  $i$  and  $j$  are the nearest neighbors and zero otherwise,  $\beta_{i_a j_b}$  is the angle made between rod  $a$  in molecule  $i$  and rod  $b$  in molecule  $j$ , and  $P_2(\cos \beta) = 3(\cos^2 \beta - 1)/2$  is the second Legendre polynomial.



**Fig. 1.** Schematic of a bent-core molecule with an electric dipole moment  $\mathbf{P} = \mu \mathbf{u}_i$ .

$U_{ij}^{\text{dd}}$  is the dipole-dipole interaction, which is usually given by

$$U_{ij}^{\text{dd}} = \frac{\mu^2}{4\pi\epsilon_0 r_{ij}^3} [(\mathbf{u}_i \cdot \mathbf{u}_j) - 3(\mathbf{u}_i \cdot \hat{\mathbf{r}}_{ij})(\mathbf{u}_j \cdot \hat{\mathbf{r}}_{ij})], \quad (3)$$

where  $\mu$  is the transverse dipole moment,  $\mathbf{u}_i$  is the unit vector along the transverse dipole moment of molecule  $i$ ,  $\hat{\mathbf{r}}_{ij}$  is the unit vector of the intermolecular separation  $\mathbf{r}_{ij}$  connecting the centers of mass of molecules  $i$  and  $j$ . However, for a lattice model, the orientations that can be adopted by the intermolecular vector are usually, by definition, discretized to the lattice axes. Lattice models that contain anisotropic interactions determined by the orientation of the intermolecular vector lead to orientationally ordered phases in which the director becomes pinned, usually along a lattice axis.<sup>[28]</sup> Therefore rather than using the full dipolar term, we use a simpler pair interaction depending merely on the relative orientation of the two

dipoles in neighboring molecules,

$$U_{ij}^{\text{dd}} = \frac{\mu^2}{4\pi\epsilon_0 r_{ij}^3} \cos \eta, \quad (4)$$

where  $\eta$  is the angle made between the dipoles for molecules  $i$  and  $j$ .

The orientation of the molecule is defined by three Euler angles  $\alpha$ ,  $\beta$  and  $\gamma$ ,<sup>[30]</sup> which is connected to the laboratory frame  $(\mathbf{X}, \mathbf{Y}, \mathbf{Z})$  with a rotation matrix. The rotation matrix is given by

$$\Omega(\alpha, \beta, \gamma) = \begin{pmatrix} \kappa_{11} & \kappa_{12} & -\sin \beta \cos \gamma \\ \kappa_{21} & \kappa_{22} & \sin \beta \sin \gamma \\ \cos \alpha \sin \beta & \sin \alpha \sin \beta & \cos \beta \end{pmatrix}, \quad (5)$$

with

$$\begin{aligned} \kappa_{11} &= \cos \alpha \cos \beta \cos \gamma - \sin \alpha \sin \gamma, \\ \kappa_{12} &= \sin \alpha \cos \beta \cos \gamma + \cos \alpha \sin \gamma, \\ \kappa_{21} &= -\cos \alpha \cos \beta \sin \gamma - \sin \alpha \cos \gamma, \\ \kappa_{22} &= -\sin \alpha \cos \beta \sin \gamma + \cos \alpha \cos \gamma. \end{aligned}$$

The unit vectors  $\mathbf{u}_1$  and  $\mathbf{u}_2$  along the two rods and the unit dipole  $\mathbf{u}$  of each molecule can all be written in terms of Euler angles,

$$\mathbf{u}_1 = \left(0, \cos \frac{\theta}{2}, \sin \frac{\theta}{2}\right) \Omega(\alpha, \beta, \gamma) \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \\ \mathbf{Z} \end{pmatrix}, \quad (6)$$

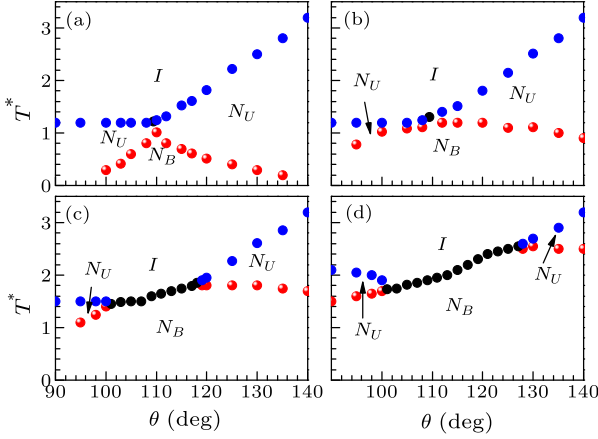
$$\mathbf{u}_2 = \left(0, \cos \frac{\theta}{2}, -\sin \frac{\theta}{2}\right) \Omega(\alpha, \beta, \gamma) \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \\ \mathbf{Z} \end{pmatrix}, \quad (7)$$

$$\mathbf{u} = (0, \cos \varphi, \sin \varphi) \Omega(\alpha, \beta, \gamma) \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \\ \mathbf{Z} \end{pmatrix}, \quad (8)$$

There are four parameters in our model: (1)  $\theta$ : the fixed angle between the two arms; (2)  $\varphi$ : the angle of molecular dipole shifting from bisector of each bent-core molecule; (3)  $\kappa = \mu^2/(4\pi\epsilon_0 r_{ij}^3 \epsilon)$ : the relative strength of dipole-dipole interaction with respect to anisotropic potential; (4)  $T^* = k_B T/\epsilon$ : the dimensionless temperature.

To explore the phase diagram of bent-core molecules with an electric dipole moment, we carried out a series of Metropolis Monte Carlo simulations.<sup>[31]</sup> All the simulations reported in this study were performed on a  $10 \times 10 \times 10$  cubic lattice under periodic boundary conditions, with each molecule assumed to interact with its six nearest neighbors, as given by Eq. (1). Each Monte Carlo step is made by selecting a site randomly and is employed to calculate the energy of this configuration ( $U_1$ ), then randomly changing its orientation and also calculating its energy ( $U_2$ ). Equilibration runs were typically of 100000 sweeps with each sweep consisting of  $N = 10^3$  Monte Carlo steps, followed by a production run of 10000 sweeps.

Longer equilibration runs are performed in the vicinity of phase transitions.



**Fig. 2.** The phase diagrams of liquid crystal formed by symmetric bent-core molecules ( $\varphi = 0$ ) as functions of bend angle  $\theta$  and temperature  $T^*$  for four different transverse dipoles: (a)  $\kappa = 0.0$ , (b)  $\kappa = 0.5$ , (c)  $\kappa = 1.0$ , and (d)  $\kappa = 1.5$ .

The orientational order of a rigid biaxial molecule in a biaxial phase can be characterized at the second rank level by a Cartesian supermatrix  $S$  with elements<sup>[25]</sup>

$$S_{ab}^{AB} = \left\langle \frac{(3l_{aA}l_{bB} - \delta_{ab}\delta_{AB})}{2} \right\rangle, \quad (9)$$

where the subscripts  $a$  and  $b$  denote the molecular axes  $x$ ,  $y$ ,  $z$ , the superscripts  $A$  and  $B$  denote the laboratory axes  $X$ ,  $Y$ ,  $Z$ ,  $l_{aA}$  is the direction cosine between the molecular axis  $a$  and the laboratory axis  $A$ ,  $\delta_{ab}$  is a Kronecker delta function, and the angular bracket denotes an ensemble average. The properties of this supermatrix were described in more detail in Ref. [25].

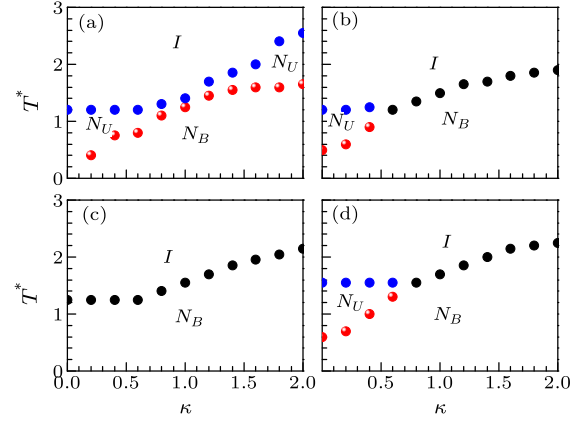
In fact, the principal axes of the phase change from configuration to configuration, and are explicitly unknown during the Monte Carlo simulation. To determine these, we use the procedure described by Vieillard-Baron,<sup>[32]</sup> in which a  $Q$  tensor is defined for setting axes in the molecule, in analogue to a diagonal matrix of  $S$ ,<sup>[25]</sup>

$$Q_{aa}^{AB} = \left\langle \frac{(3l_{aA}l_{aB} - \delta_{aa})}{2} \right\rangle, \quad (10)$$

where  $a$  denotes the axis set in the molecule,  $A$  and  $B$  denote an arbitrary laboratory frame  $X'$ ,  $Y'$  and  $Z'$ . The matrix is then diagonalized and the resulting eigenvectors give the orientations of the directors. The three eigenvalues,  $Q_{aa}^{AA}$  ( $A = X, Y, \text{ or } Z$ ), are the order parameters of axis  $a$  with respect to the directors, and the largest order parameter is chosen to be denoted by  $Q_{aa}^{ZZ}$ . Here it should be noted that  $Q_{aa}^{XX} = Q_{aa}^{YY} = -Q_{aa}^{ZZ}/2$  defines a uniaxial phase,  $Q_{aa}^{XX} = Q_{aa}^{YY} = Q_{aa}^{ZZ} = 0$  corresponds to an isotropic phase, and  $Q_{aa}^{XX} \neq Q_{aa}^{YY} \neq Q_{aa}^{ZZ} \neq 0$  gives a biaxial phase. Therefore, the phase of the system can be determined according to the three eigenvalues.

The phase behaviors of biaxial bent-core liquid crystal were investigated as functions of bend angle

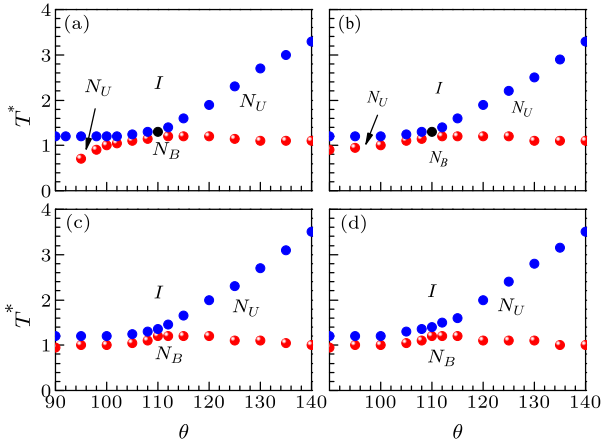
$\theta$ , relative dipole-dipole strength  $\kappa$ , dipole moment deviation angle  $\varphi$ , and dimensionless temperature  $T^*$  using Monte Carlo simulations. In a previous study of bent-core molecules,<sup>[25]</sup> the order parameters for the arm axes were found to possess the most useful information on phase behaviors, which are also used in our dipolar model. Different phases as well as transition temperatures are identified from the behaviors of order parameters.



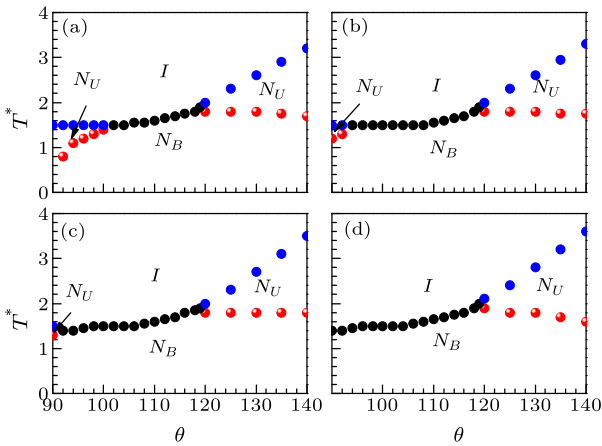
**Fig. 3.** The phase diagrams of liquid crystal formed by symmetric bent-core molecules ( $\varphi = 0$ ) as functions of temperature  $T^*$  and dipole strength  $\kappa$  for four different bend angles: (a)  $\theta = 95^\circ$ , (b)  $\theta = 105^\circ$ , (c)  $\theta = 109.47^\circ$ , and (d)  $\theta = 115^\circ$ .

The phase diagram in terms of  $\theta$  and  $T^*$  is plotted for four different values of  $\kappa$ , as shown in Fig. 2, when the dipole moment is in the direction of bend angle bisector ( $\varphi = 0$ ). When  $\kappa = 0$ , as shown in Fig. 2(a), the uniaxial nematic phases were separated into two regions by a biaxial nematic phase. The Landau point where the liquid crystal undergoes a transition from an isotropic phase directly to a biaxial nematic one is found at the tetrahedral angle of  $\theta = 109.47^\circ$  ( $\cos^{-1} \theta = -1/3$ ), which is in good agreement with the prediction by molecular field theory.<sup>[23]</sup> If the dipole-dipole interaction is taken into account, such as  $\kappa = 0.5$  (Fig. 2(b)), the  $N_U$ - $N_B$  phase transition temperature increases apparently, indicating that uniaxiality is suppressed by biaxiality. When  $\kappa$  increases up to 1.0, the phase diagram (Fig. 2(c)) is found to change substantially, where it is found that  $I$ - $N_B$  transition occurs not just at a single Landau point but at a range of angles ( $101^\circ$ – $119^\circ$ ). This is also called the Landau line, indicating that strong dipolar interaction (or large dipole moment) enhances biaxiality. As the interaction is further increased, such as  $\kappa = 1.5$ , one can see a similar phase diagram (Fig. 2(d)), where the Landau line ranges from  $101^\circ$ – $127^\circ$ . The results shown here are in accordance with those of Bates.<sup>[28]</sup>

The phase diagram in terms of  $\kappa$  and  $T^*$  is also plotted in Fig. 3 for four different bend angles. For  $\theta = 95^\circ$  (Fig. 3(a)), there exists no  $I$ - $N_B$  transition, while for  $\theta = 109.47^\circ$  (Fig. 3(c)), only the  $I$ - $N_B$  transition is found, indicating that this is a Landau point.



**Fig. 4.** The phase diagrams of liquid crystal formed by bent-core molecules with an electric dipole moment  $\kappa = 0.5$  as functions of temperature  $T^*$  and bend angle  $\theta$  for four different deviation angles: (a)  $\varphi = 0^\circ$ , (b)  $\varphi = 5^\circ$ , (c)  $\varphi = 10^\circ$ , and (d)  $\varphi = 15^\circ$ .



**Fig. 5.** The phase diagrams of liquid crystal formed by bent-core molecules with an electric dipole moment  $\kappa = 1.0$  as functions of temperature  $T^*$  and bend angle  $\theta$  for four different deviation angles: (a)  $\varphi = 0^\circ$ , (b)  $\varphi = 5^\circ$ , (c)  $\varphi = 10^\circ$ , and (d)  $\varphi = 15^\circ$ .

For the other two bend angles,  $I-N_U$ ,  $N_U-N_B$  and  $I-N_B$  all exist. From the figure, it is also found that as the dipole strength  $\kappa$  increases, the phase transition temperature increases and the appearance of biaxial nematic phase is encouraged.

It is more interesting to find out whether or not the electric dipole moment fall into the direction of the bent-core angular bisector. The phase diagrams of liquid crystal formed by bent-core molecules with a deviating electric dipole moment  $\kappa = 0.5$  in terms of temperature  $T^*$  and bend angle  $\theta$  for four different deviation angles are shown in Fig. 4. For small deviation angles, such as  $\varphi = 5^\circ$  (Fig. 4(b)), there still exists a Landau point at the tetrahedral angle of  $\theta = 109.47^\circ$ . As the deviation angle is further increased to  $\varphi = 10^\circ$  (Fig. 4(c)), one sees the disappearance of the Landau point, but the uniaxial phase for small bend angles is squeezed, indicating that in this regime, it becomes more difficult to form a uniaxial structure, which can also be seen from Fig. 4(d) when  $\varphi = 15^\circ$ .

When the dipole moment strength is increased to 1.0, phase diagrams for the four different deviation angles are presented in Fig. 5, where a Landau line ranging from  $\theta = 94^\circ$  to  $\theta = 119^\circ$  is found for the deviation angle  $\varphi = 5^\circ$  (Fig. 5(b)). At the deviation angle  $\varphi = 10^\circ$  (Fig. 5(c)), it is found that biaxial phase is encouraged for small bend angles. As the deviation angle is further increased to  $15^\circ$  (Fig. 5(d)), one finds a longer Landau line and the uniaxiality is completely suppressed in this small bend-angle regime.

In summary, a series of Monte Carlo simulations have been performed based on a dipole model for bent-core molecules. Simulation results show that liquid crystals formed by bent-core molecules with strong dipolar interaction do not exhibit the classical phase diagram predicted by theory. Strong dipolar interaction enhances the system biaxiality while the deviation of the dipole moment from its angular bisector of bent-core molecules suppresses uniaxiality in the small-bend angle regime.

It should be noted that in our model, bent-core molecules are restricted to lattice sites and the effect of translational order is neglected. In addition, molecular features such as flexibility and conformational changes may also play an important role in a realistic biaxial nematic system.

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